5-2015

Synthesis of Diazonium Perfluoroalkyl(Aryl) Sufonimide (PFSI) Zwitterions for Solid Acid Alkylation Catalysts

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A thesis presented to the faculty of the Department of Chemistry at East Tennessee State University

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In partial fulfillment for the requirements of the degree

Bachelor of Science in Chemistry

Dr. Hua Mei, Advisor

Dr. Cassandra Eagle, Chair

Dr. Onyango

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By

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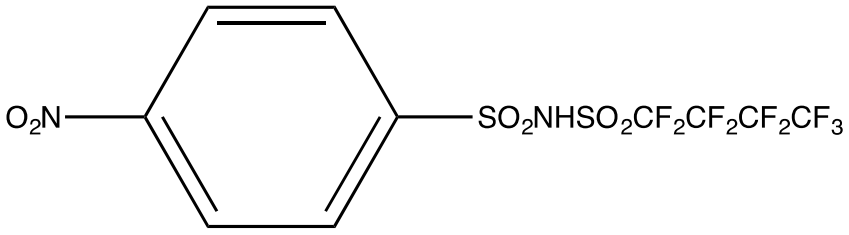
ABSTRACT

The final objective of this project is to create an environmentally friendly solid alkylation catalyst to replace the commercially available liquid acid catalysts, such as hydrofluoric acid and sulfuric acid, which are used in the petroleum industry. My research target is to synthesize the diazonium PFSI zwitterions, which can be chemically grafted on the silica as the solid alkylation catalyst. A 4-steps synthesis is designed to prepare the diazonium PFSI zwitterions. The first two steps were successfully completed in the lab. The first one is to prepare the starting material of 4-nitrobenzenesulfonamide from an ammonolysis reaction between 4-nitrobenzene sulfonyl chloride and ammonium hydroxide. And next, a base catalyzed coupling reaction was carried out with 4-nitrobenzenesulfonamide and commercially available perfluorobutane sulfonyl fluoride with nitrogen gas (N_2) protection. The coupling product (I in Figure 1) was then purified by extraction and recrystallization. All chemicals in the synthesis procedure were characterized with proton NMR, fluorine NMR, Infrared (IR) spectroscopy and melting points.

Figure 1: Compound I (*p*-$NO_2PhSO_2NHSO_2C_4F_9$)



I

INTRODUCTION

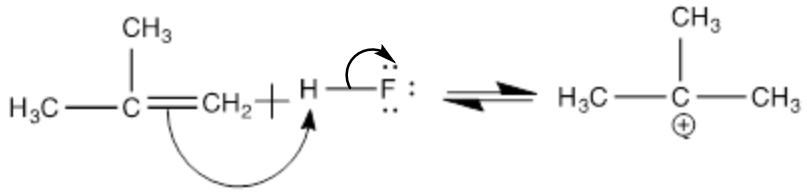
Preface

Catalysts are chemicals that can increase the rate of a reaction by lowering the activation energy and alkylation catalysts specifically target reactions that lead to the addition of alkyl groups to molecules.[1] Catalytic alkylation has been researched since the 1930s, with Ipatieff and Grosse performing the alkylation of Isobutane with ethene using aluminum chloride ($AlCl_3$) and hydrochloric acid as a catalyst.[2]

In the following scheme, a generic reaction mechanism is shown in which the reaction of the isobutane and 2-butene that is catalyzed by a hydrogen fluoride (HF). It demonstrates how an acidic catalyst can assist this alkylation reaction:

Scheme 1: Reaction Mechanism of Isobutane and 2-butene with a liquid acid catalyst.

1)



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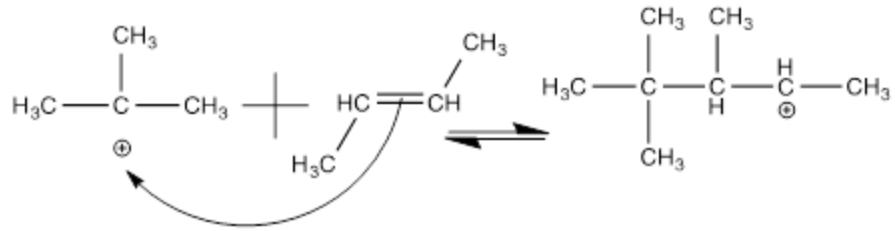

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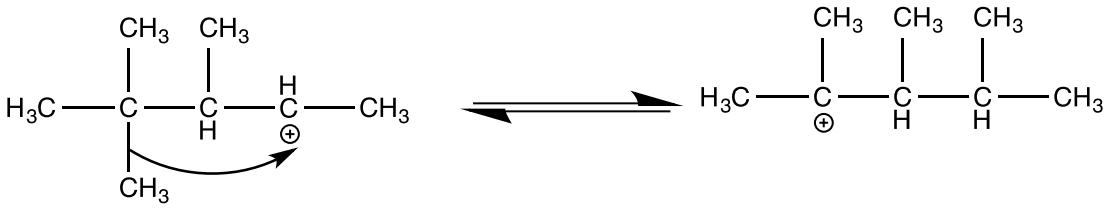

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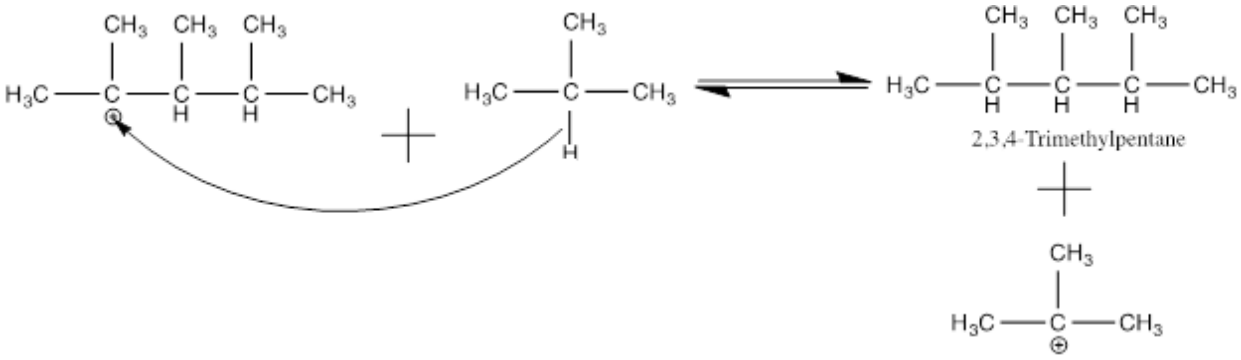
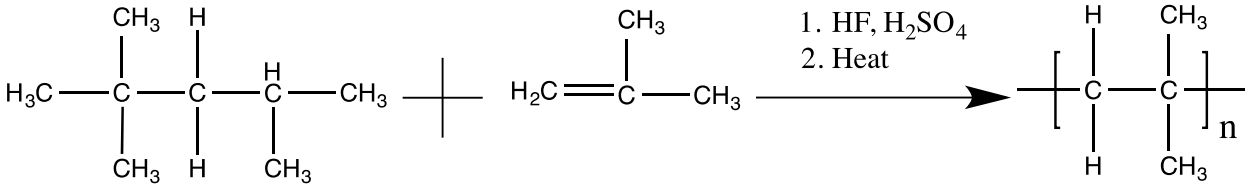


The mechanism by which the reaction occurs is consecutive and involves carbocation intermediates.[3] The steps include addition, dimerization, isomerization and hydride shift. It begins with the reaction of the isobutane with the acid to form the isobutane cation, which is added to the olefin (2-butene). The next step involves a methyl shift that isomerizes the molecule. Lastly, a hydride transfer results in the formation of the desired isooctane.[4] An issue that affects the production of the isooctane product is formation of the non-desired compound, polyisobutylene.[5] The following scheme displays this side-reaction:

Scheme 2: Formation of Polyisobutylene.



According to the literature, it is suggested that the formation of different isomers is due to the acid-catalyzed rearrangement of the isooctane carbocation.[4]

During World War II, the use of liquid acid catalysts, such as hydrofluoric and hydrochloric acid, became predominant due to the need for a production of a great amount of aviation fuel and high-quality blending gasoline.[5] Until now, these catalysts are widely used in the petroleum alkylation industry.[6] Dr. Corma and Martinez stated that these liquid catalysts are harmful for humans due to their volatility.[5] The employees can be injured when they come in contact with the volatile fumes.[5] This factor creates an occupational hazard with liquid catalysts. Along with the safety of the employees, liquid acid catalysts can also affect the safety of the environment. The processes involved with this catalyst focus on product yield. They ignore the environmental impact of the corresponding formation of the inorganic waste and the toxic byproducts.[7] These are harmful to the environment. But, the major advantage of liquid catalysts is their high isooctane production efficiency.[5]

Solid acid catalysts have been studied since the 1960s with the initial research being performed by the Mobil Corporation on a variety of zeolites.[8] The most predominantly used solid acid catalysts are zeolites series and Lewis acids.

The following **table 1** lists the main advantage and disadvantages associated with solid acid catalysts.[5, 9]

Table 1: Advantages and Disadvantages of Common Solid Acid Catalysts

	Zeolite Series Catalyst	**Lewis Acid Catalyst**
Advantages	Less or no corrosion	Environment friendly
	No waste or disposal problems	
	Easy set-up of continuous processes in fixed bed reactions	
	High thermostability	
	Great adaptability	
Disadvantages	Sensitivity to deactivation	Produces strong acids during reaction
	Microporisity prevents the formation of bulky compounds	Leads to metal contaminated streams
	Decays quickly under catalysis	Not selective

Other solid materials that were found by the same corporation to have some catalytic properties included Hydrofluoric acid-Antimony pentafluoride on fluorided alumina and Boron trifluoride modified amberlyst-15.[8] Some of those catalysts have reached the pilot plant stage, such as antimony pentafluoride on acid washed silica.[8] In summary, the alkylation catalysts are made of two main components: acid and porous solid.[5]

Meanwhile, researchers are exploring newer options for solid acid alkylation catalysts that could be environment friendly, more efficient, and also less expensive.[8] The objective of our research is to prepare a series of novel alkylation catalysts, which are the porous inorganic solid modified by diazonium perfluoroalkyl(aryl) sulfonimide (PFSI) zwitterions. According to Kirsch, PFSI is a super acid not only due to strongly electron withdrawing perfluoroalkyl group, but also because of the resonance stabilization of the sulfonimides.[10, 11] PFSI has an acid dissociation constant (pK_a) of 0.91.[12] Another unique characteristic of PFSI molecules is the delocalization of charge in their conjugate bases; this factor also increases the acidity of

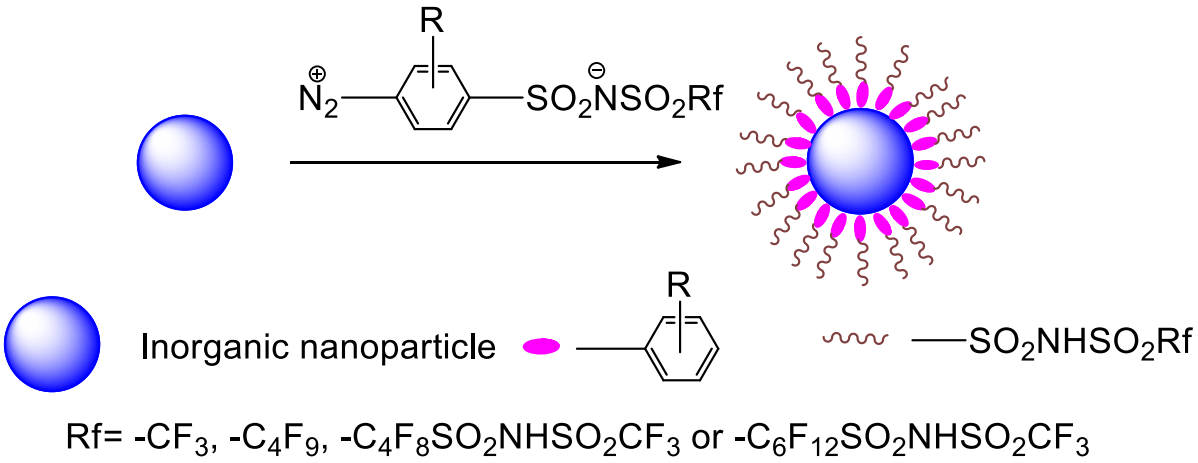
perfluoroalkyl sulfonimides.[13] PFSI compounds are not only a super acid but also contain other properties such as chemical and physical stability.[14] The PFSA compounds are acidic and also are chemically inert. This prevents any occurence of dehydration and oxidation reactions.[14] Furthermore, diazonium moiety will bind the PFSI acids to the porous inorganic solids via covalent bonds.

The designed alkylation catalysts will be prepared from diazonium PFSI zwitterions. The Diazonium salt has two nitrogen atoms joined together in a positive ion.[15] Diazonium compounds are usually not stable because the nitrogen is a good leaving group.[16] It is also important to note that most diazonium salts are energetic materials and are unstable as solids at room temperature and this includes benzenediazonium chloride and benzene diazonium sulfate.[17] The aromatic diazonium zwitterions used in our planned catalyst are more stable than regular diazonium compounds due to the big size of the molecule.[18] Moreover, zwitterions, as inner salts, are more stable than outer salts.[19] A zwitterion is a molecule that has both a positive and a negative charge and are both a cation and an anion leading to the term hybrid.[11] The presence of a filled orbital on one atom and an unfilled orbital on another atom of the same molecule causes inductive distortion by a charge separation of the orbitals that may sometimes be conjugated.[20] The molecule can be classified as semipolar. The diazonium PFSI zwitterions are designed to be grafted onto silica or an alumina surface via diazonium chemistry. Diazonium chemistry refers to the study of the reactivity of diazonium salts. They are important intermediates and react with nucleophiles through the loss of nitrogen.[21]

In our research, inorganic nanoparticles, such as silica and alumnia nanoparticles will be the ideal supports for PFSI acid coating due to their large surface area. A nanoparticle is any particle with a dimension between 1 and 100 nanometers.[22] For example, the specific surface area of

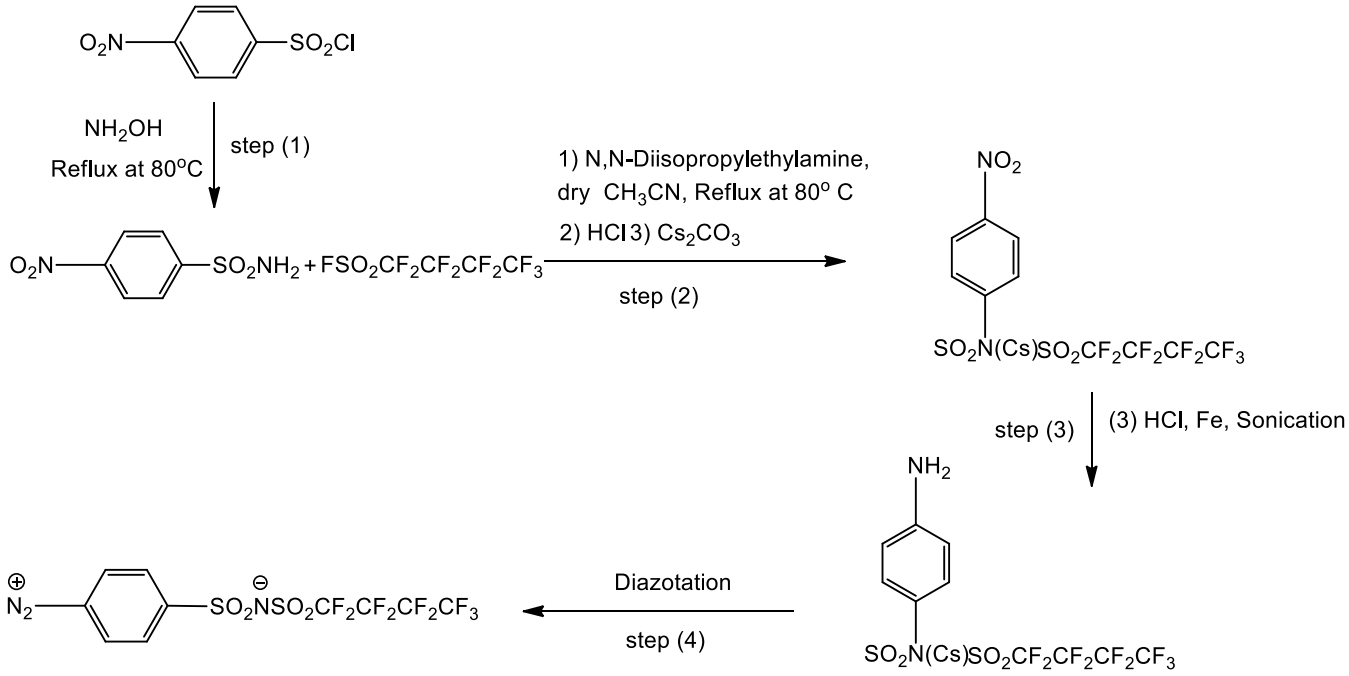
commercial “Aerosol 200” silica nanoparticles is around 200 m^2/g when measured on the transmission electron microscope.[23] The high surface area of nanoparticles allows it to be modified with diazonium zwitterionic salts. The thermal stability of nanoparticles will also allow them to work at high temperatures.[24] The next diagram lays out the formation of the hypothetical bond between the zwitterions and the nanoparticle.

Scheme 3: Attachment of catalyst to silica nanoparticles.



The whole synthesis route for diazonium PFSI zwitterions is designed as **Scheme 4**.[25] There are in total 4 steps involved in the preparation, which includes (1) ammonolysis, (2) coupling, (3) reduction, and (4) diazotation. So far, the first two steps have been carried out. The coupling product needs further purification. After that, the reduction and diazotation will be completed to obtain the first target diazonium PFSI ziwtterionic compound.

Scheme 4: Overall Synthesis Scheme.[25]

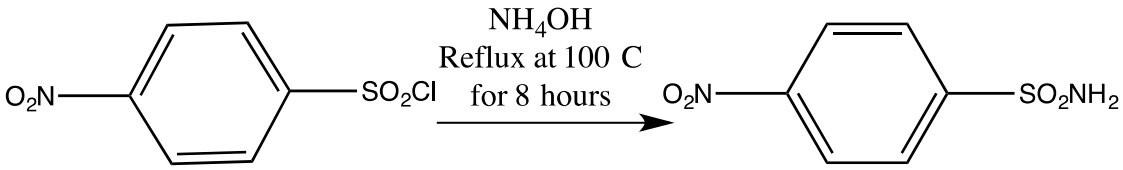


RESULTS AND DISSCUSSION

Ammonolysis

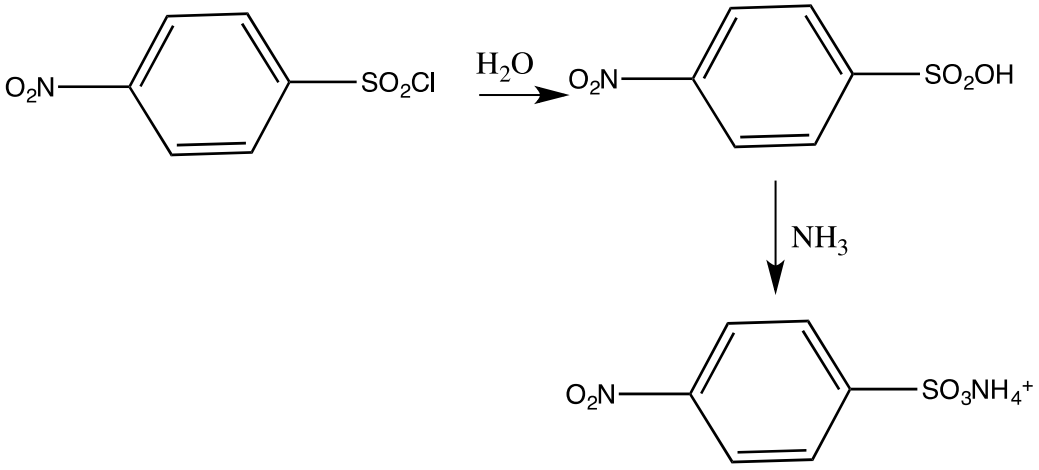
The ammonolysis reaction is a typical S_N2 reaction. An S_N2 reaction is a bimolecular substitution reaction between a nucleophile and a substrate.[1] In the ammonolysis reaction, the halogen (here it is the chloride) is replaced with an $–NH_2$ group.[26] Although ammonia is a better nucleophile than water, hydrolysis is the competing reaction while the ammonolysis occurs to the p-nitrobenzenesulfonyl chloride.

Scheme 5: Reaction Scheme of Ammonolysis.



The 5th scheme shows the hydrolysis reaction between starting material aromatic sulfonylchloride and water. The hydrolysis impurities can be easily removed by vacuum filtration since it can be dissolved in water

Scheme 6: Formation of Hydrolysis impurity in Ammonolysis Reaction.

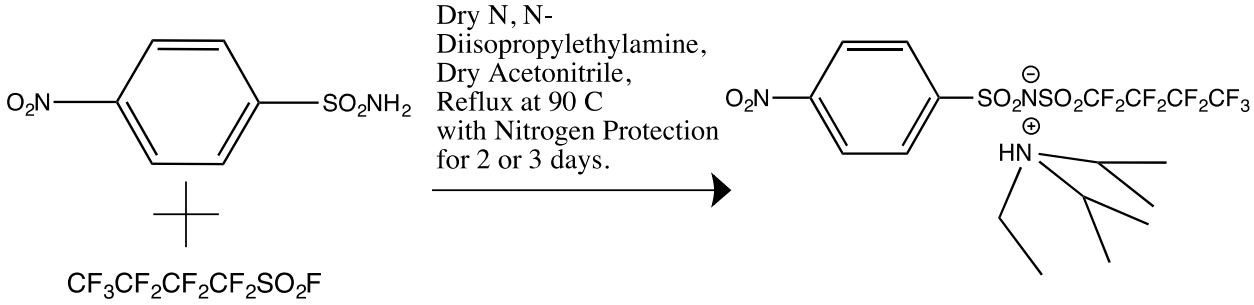


For the ammonolysis procedure, the yield is not great. The possible reasons are weight loss during transfer of the product and the unavoidable formation of a hydrolysis by product.

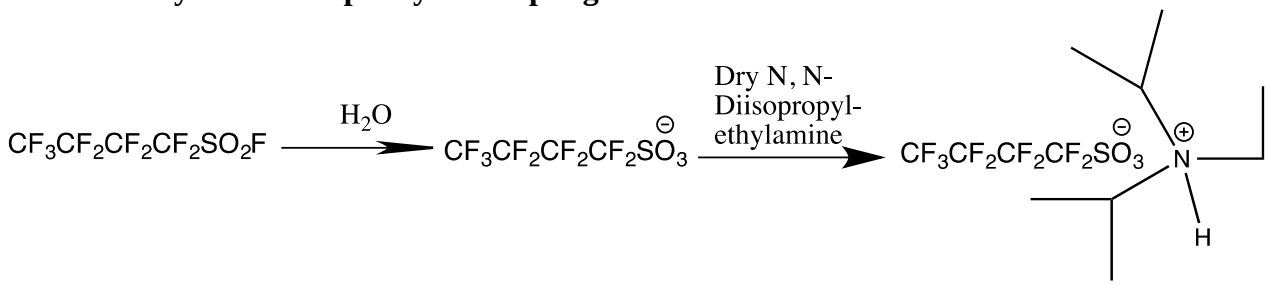
Coupling Reaction

The coupling reaction is also a S_N2 reaction. Since p-nitrobenzene sulfonamide is not a strong nucleophile, the base Diisopropyl ethylamine (DIEA) converted SO_2NH_2 to SO_2NH^- as a stronger nucleophile. The ratio of these reactants, p-nitrobenzene sulfonamide to nonafluorobutane sulfonyl fluoride, is 1:1.02. Even if a small amount of nonafluorobutane sulfonyl fluoride is consumed, excess reagent will allow enough sulfonyl fluoride to react with the sulfonyl amide. The 7th scheme represents how the hydrolysis impurity formed from perfluoroalkylsulfonyl fluoride. The coupling product needs to be further purified since it still contains hydrolysis impurity.

Scheme 7: Reaction Scheme of Sn2 Carbon coupling reaction.



Scheme 8: Hydrolosis Impurity of Coupling Reaction.

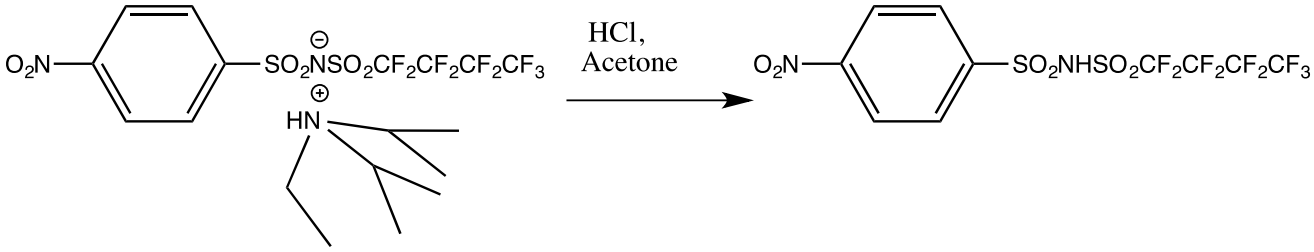


The coupling reaction was successfully carried out according to fluorine NMR. The disappearance of the sulfonyl fluoride peak around 55.0 ppm in proton NMR (Appendix H) of the starting material of nonafluorobutane sulfonyl fluoride proved that it had reacted with the 4-nitrobenzene sulfonamide.

Furthermore, the IR spectrum (Appendix D) of this compound displays peaks for the nitro group at 1537.27cm^{-1} and 1296.16 cm^{-1}. Moreover, there is no amine peak around 3300 cm^{-1}, which is present in the IR spectrum of the starting material, 4-nitrobenzene sulfonamide (Appendix C). All the detailed information from spectra assists us in identifying the product.

Nevertheless, according to fluorine and proton NMR (Appendices F and G), the crude product still contains hydrolysis impurity and DIEA catalyst. Therefore, the further purifications are necessary to obtain the pure coupling product.

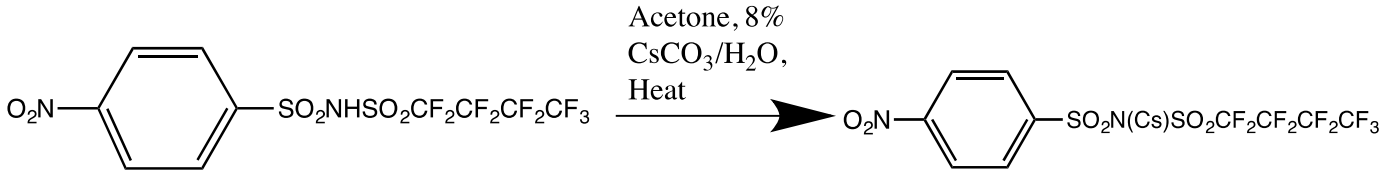
Scheme 9: Acidification of the Hydrolysis impurity by-product.



First purification carried out is the acidification process. The purpose of acidification is to convert all salts into acidic form. Hence, the DIEA can be removed by solvent-solvent extraction. After acidification, the disappearance of DIEA peaks in the proton NMR spectrum of the coupling product proves the completed conversion.

Recrystallization

Scheme 10: Recrystallization of Coupling Compound with Cesium Salt.



Next, the coupling product is transformed into the Cesium salt to remove the hydrolysis impurities of nonafluorobutane sulfonyl fluoride. Two solvents (1:1 ratio of acetone to water) recrystallization is performed. After all, the pure coupling product was obtained with limited

yield. The possible issues associated with yield include using too much solvent or cooling the solution too fast after heating.[27]

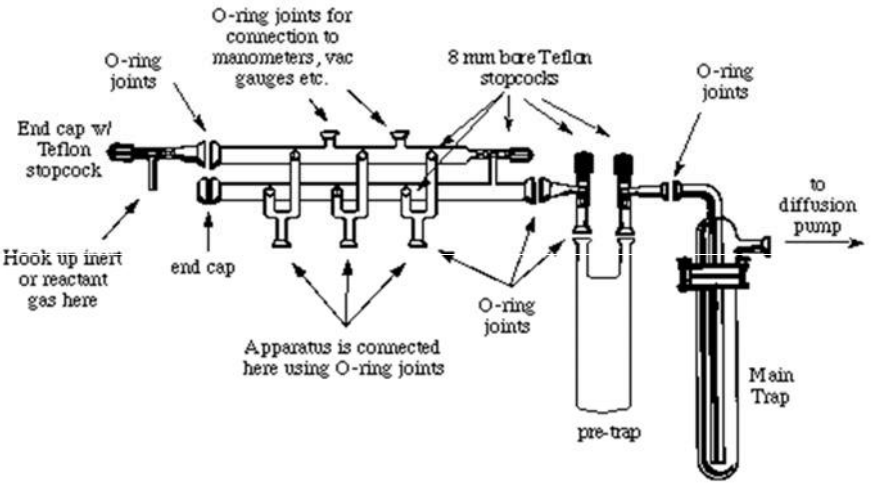
EXPERIMENTAL

General Considerations

^{1}H and ^{19}F NMR spectroscopy were carried out on the Joel JNM-ECP 400 MHz FT NMR. Chemical shifts were reported in parts per million (ppm). The coupling constants or 'J' value were reported in Hz. For the ^{1}H NMR, the spectrum was referenced with tetra methyl silane (TMS) external standard. In the ^{19}F NMR spectrum, the spectrum was referenced to the trichlorofluoromethane ($CFCl_3$) external standard. The splitting patterns of resonance were described as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m).

The infrared spectra were recorded using a Thermo Electron Corporation's Nicolet 380 FI-IR Spectrometer. The samples were prepared as a fine solid powder. The Infrared spectra were reported in wavenumbers (cm^{-1}) and were scanned from 4000 cm^{-1} to 450 cm^{-1}. In reporting the spectra, intensity abbreviations were also used: vs (very strong), s (strong), m (medium), w (weak), and vw (very weak).

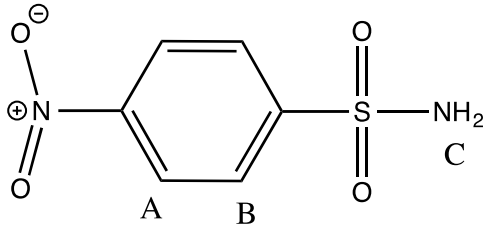
Figure 2: 2-manifolds glass vacuum line.[28]



Synthesis of 4-nitrobenzenesulfonamide from 4-nitrobenzenesulfonyl chloride

2.00 grams (0.00902 mol) of 4-nitrobenzene sulfonylchloride and 20 mL (0.508 mol) of 28-30% ammonia hydroxide were mixed in a 250 mL round bottom flask along with 5 mL of acetonitrile. This mixture was refluxed for 8 hours at 100 ^{o}C**.** TLC revealed one spot with Rf values of 0.74 (product) with the 1:1 hexane to acetone solvent. After removing the solvent, the product was vacuum filtered out and vacuum dried overnight. 1.177 grams of product was obtained with yield of 65.39%.

Figure 3: 4-nitrobenzene Sulfonamide.



Melting Point:- 180.6 ^{o}C to 182.4 ^{o}C.

^{1}H NMR (400 MHz; CD3CN; ppm): δ_A 8.35 (2H, d), δ_B 8.05(2H, d), J_{AB} = 8 Hz, δ_C 5.94 (2H, s).

IR (ν_{max}/cm^{-1}): 3331.07m (NH), 1516.05s and 1316.60s (NO), 1161.15s and 1138s (S=O).

Gas Chromatography/Mass Spectrum Peak:- 203 g/mol

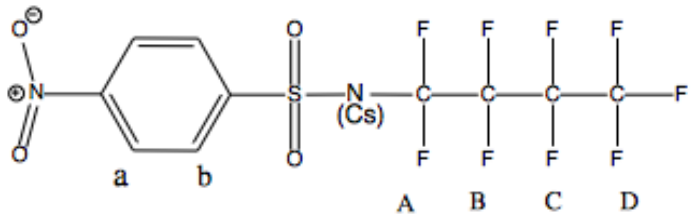
Synthesis of p- $NO_2PhSO_2N(Cs)SO_2C_4F_9$

In the glove box, 1.52 g (0.00504 mol) of nonafluorobutane sulfonyl fluoride was added in a three-necked round bottom flask first. And then, 1.00 g (0.00494 mol, 1.02:1. ratio) of 4-nitrobenzenesulfonamide was added. After that, 22.6 ml of dry acetonitrile and 3.4 ml of dry DIEA were injected into the flask subsequently. The solution mixture was then refluxed at 90 ^{o}C under nitrogen gas protection for 3 days. The reaction was monitored with fluorine NMR. After the reaction had completed, the solvent was removed with a rotary evaporator and the solid was vacuum dried overnight.

Next, the crude product was re-dissolved in 4 mL of acetone and 1 mL of concentrated HCl. The mixture was left overnight in the acidic medium that had a pH of 2. The acetone was removed with a rotary evaporator again. Afterwards, the solid was dissolved in 5 ml ethyl acetate and washed three times with 5 mL of Brine water.

The crude coupling product was then recrystallized with 0.8 grams cesium carbonate (2.45 mmoles) in 10 ml of water and 10 ml of acetone at boiling temperature for 20 minutes. The precipitate solution was cooled down and then left overnight in the refrigerator. The purified product was filtered with 3 X 10 ml of cold water and dried overnight in the hood. The 1.33 grams of pure coupling product was obtained with yield of 41.84%.

Figure 4: p- $NO_2PhSO_2N(Cs)SO_2C_4F_9$.



^{1}H NMR: (400 MHz; CD3CN; ppm): δ a 8.20 (2H,d), δ b 8.02 (2H,d), J_{ab} = 8 Hz

^{19}F NMR: (400 MHz; CD3CN; ppm): δ A -113.68 (2F,s), δ B -121.70 (2F,s), δ C -126.67 (2F,s), δ D -81.81 (3F,s).

IR (ν_{max}/cm^{-1}): 1537.27m and 1296.16m (NO), 1138.00vs (CF_2), 1064vs, 1122.57vs and 1288.45w (S=O).

CONCLUSION

The desired coupling product was obtained with a small amount of impurity. In order to improve the experiment, certain keys are followed for each process. In the first step, the ammonolysis reaction is susceptible to the formation of an undesired hydrolysis impurity. These traces of impurity lower the quality of the product and need to be separated using purification. Meanwhile, in the coupling reaction, the use of a strongly nucleophilic catalyst helped the substrates to react to form the coupling product. The hydrolysis reaction competes with the coupling reaction and consumes the fluorinated monomer. In the experiment, the methods of preventing hydrolysis included performing the experiment in the glove box with phosphorous pentoxide (P_2O_5) and using calcium chloride ($CaCl_2$) molecular sieves to dehydrate the reagents.

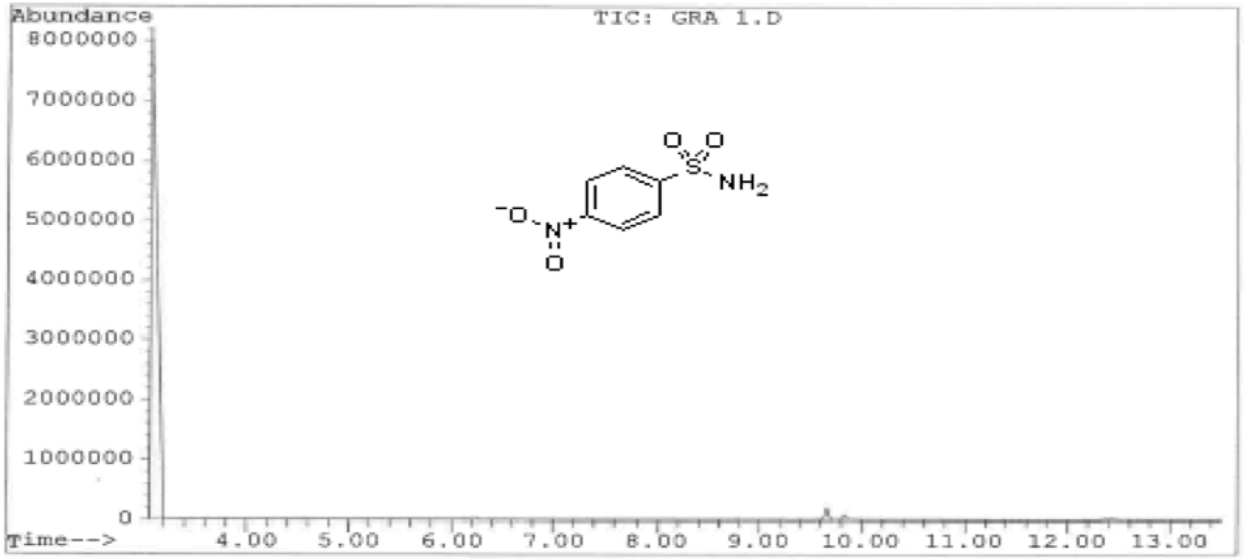
Also, proper purification is critical in this experiment since the hydrolysis impurity of the coupling reaction forms in any case. Ideally, in recrystallization, the product should dissolve in the solvent at high temperatures while the impurity remains insoluble at all temperatures of the solvent. The impurity can then be filtered out of the solvent solution.

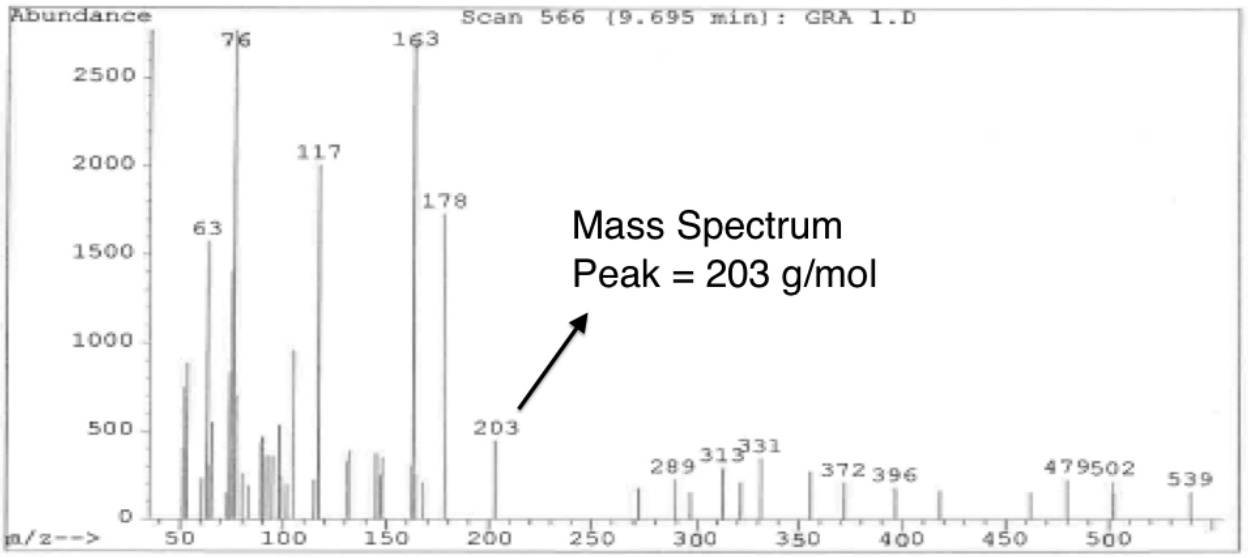
FUTURE WORK

In the future, the yield of the first and second steps needs to be improved. Changes to the purification and extraction processes can help achieve this goal. These changes could include the use of a different solvent for extraction. Meanwhile, recrystallization can be improved with the aforementioned alteration of the solvent ratio. Along with these changes, column chromatography can be implemented for purification. This method can remove impurities from the chemical mixture following the recrystallization procedure. Afterwards, reduction and diazotization will be performed to obtain the simple diazonium PFSI zwitterion: p-$N_2^+PhSO_2N^-SO_2C_4F_9$.

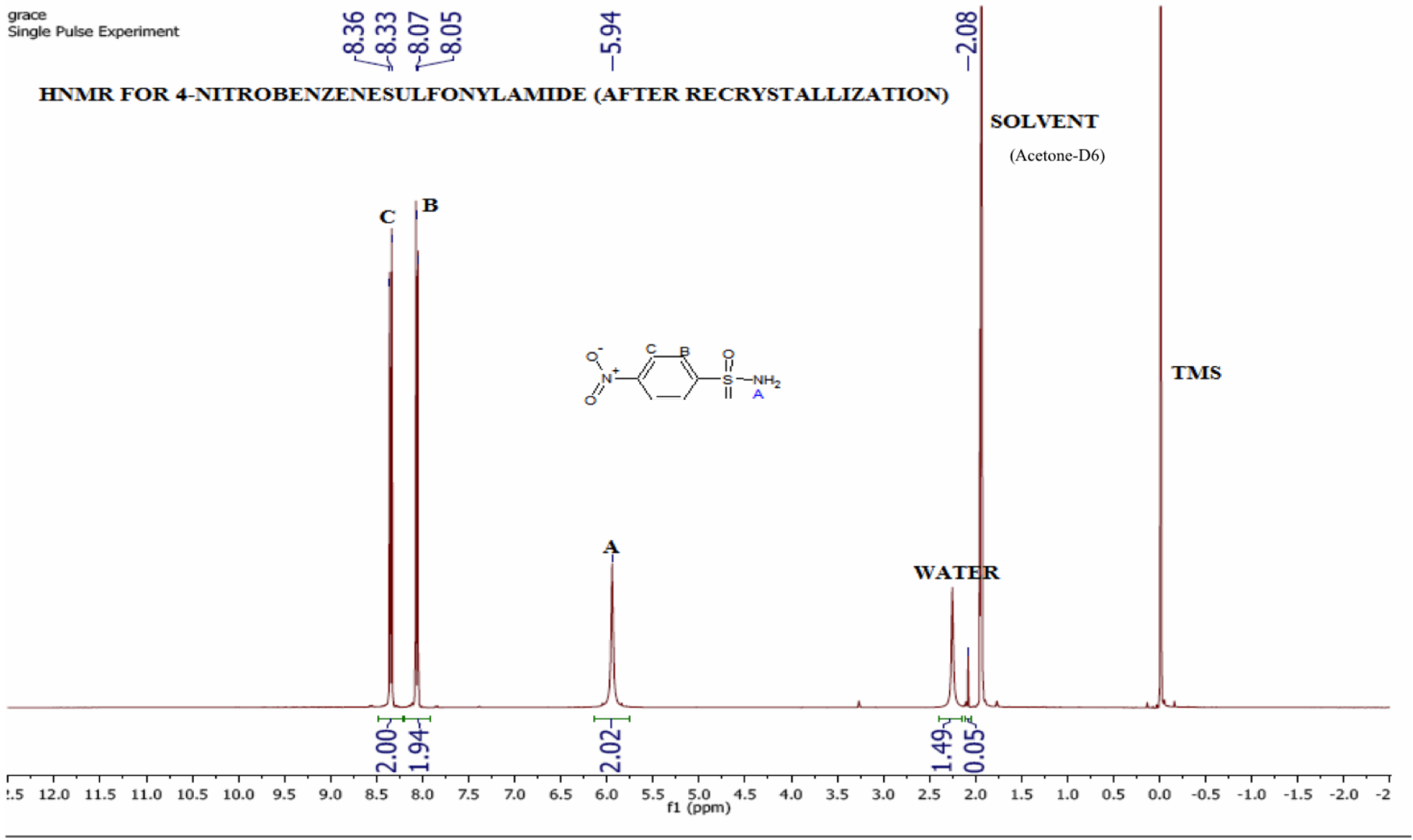
APPENDICES

APPENDIX A: THE GC/MS SPECTRUM OF 4-NITROBENZENE SULFONAMIDE.[29]

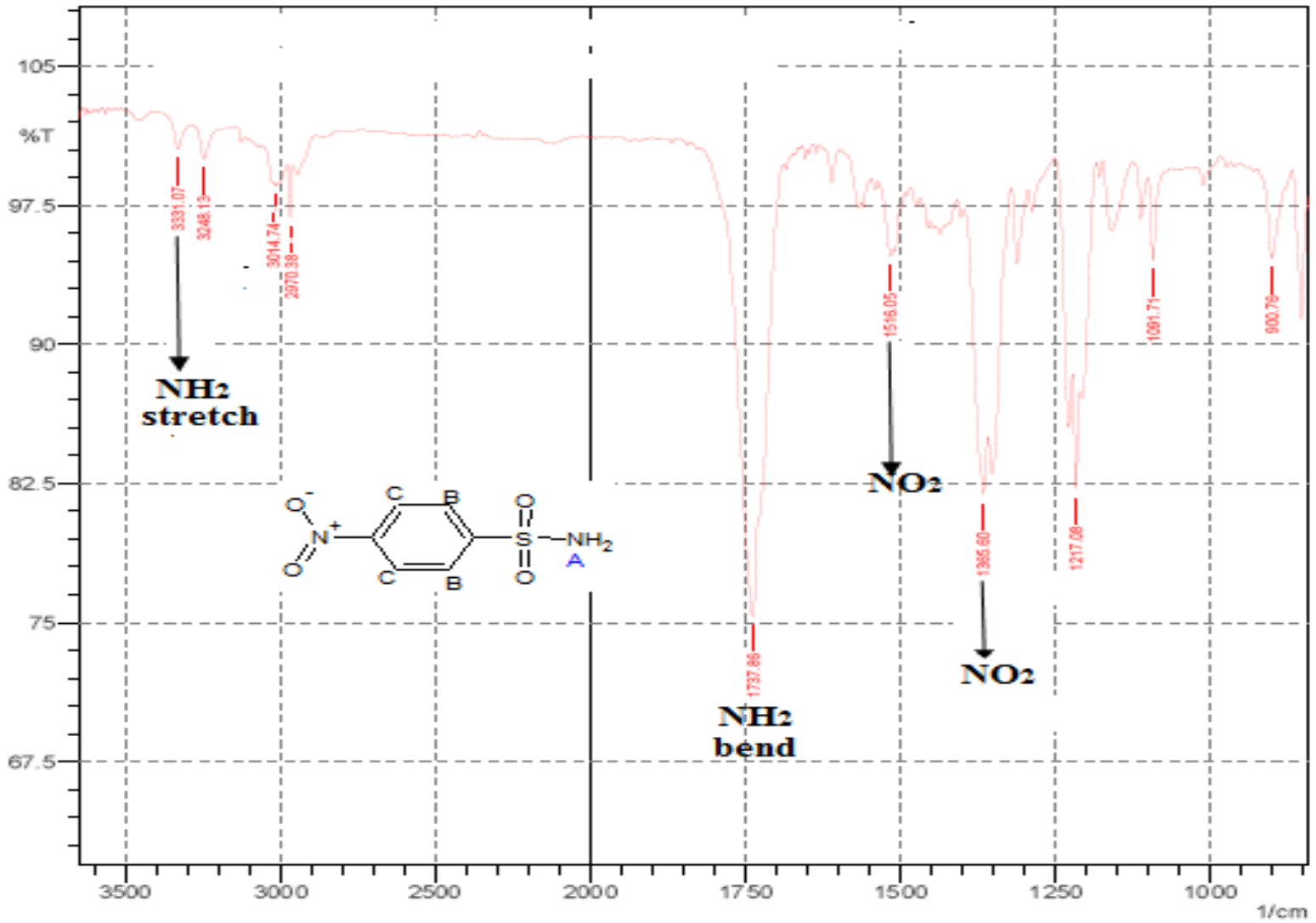




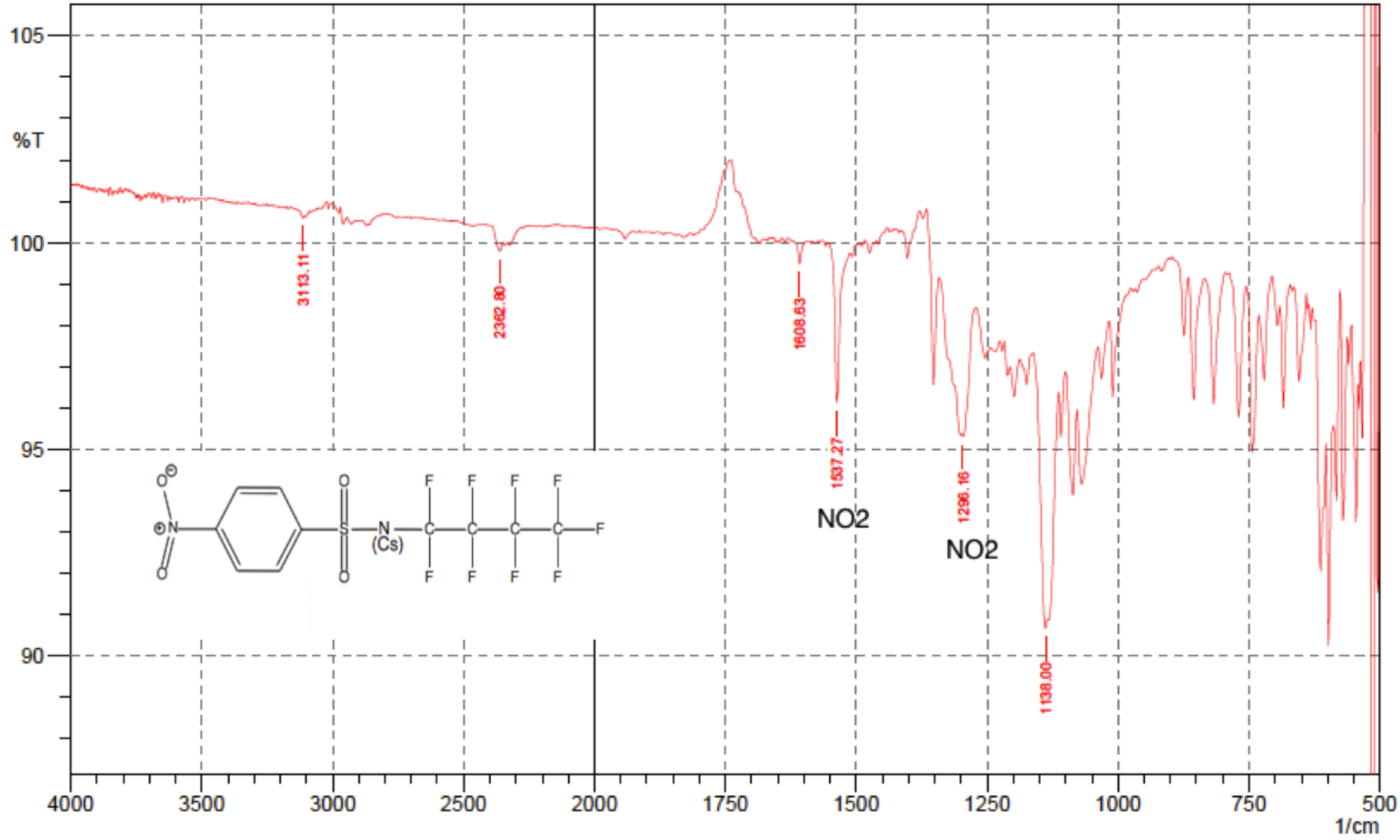
APPENDIX B: NMR SPECTRUM OF 4-NITROBENZENE SULFONAMIDE.[28]



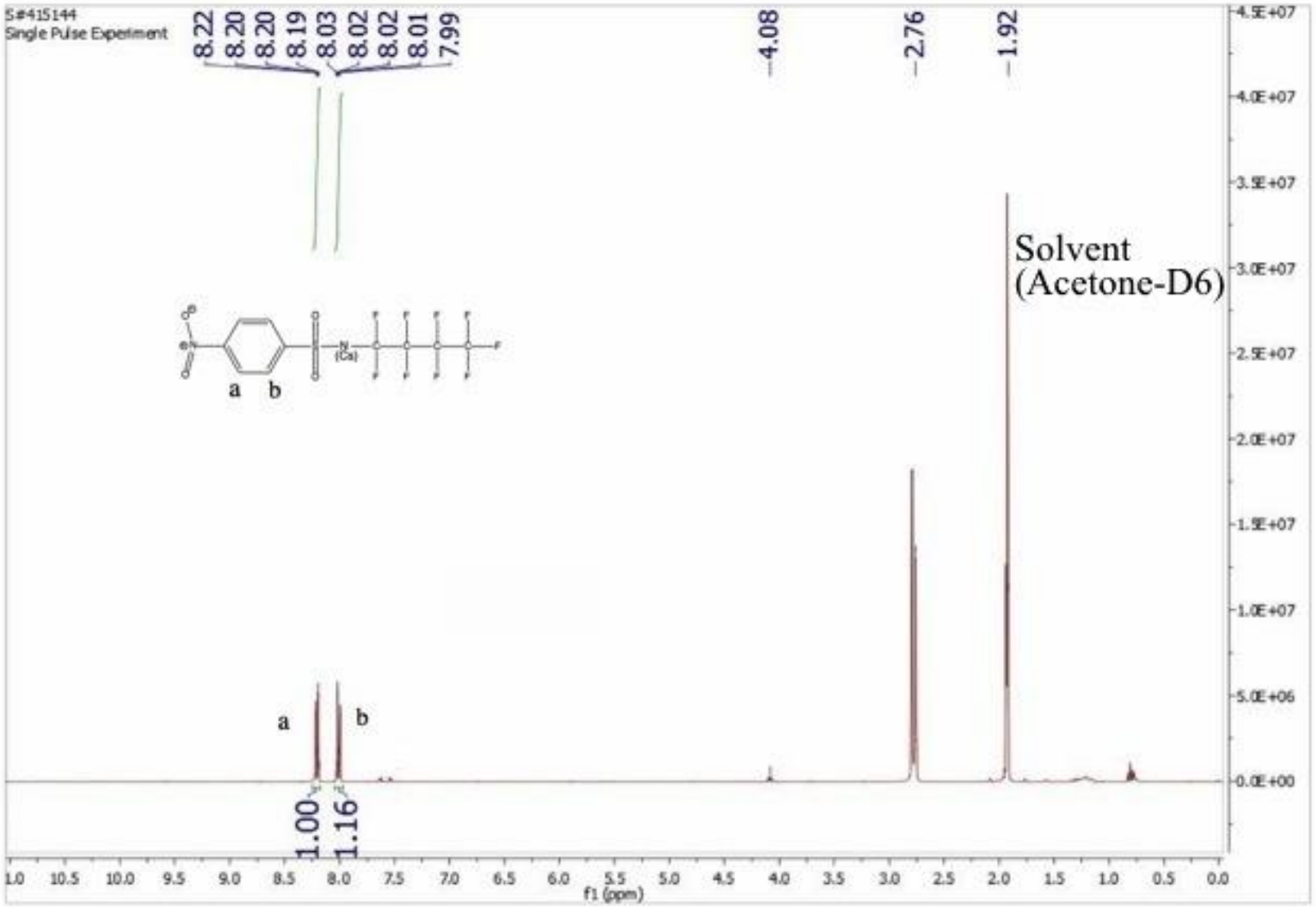
APPENDIX C: IR SPECTRUM OF AMMONOLYSIS PRODUCT.[28]



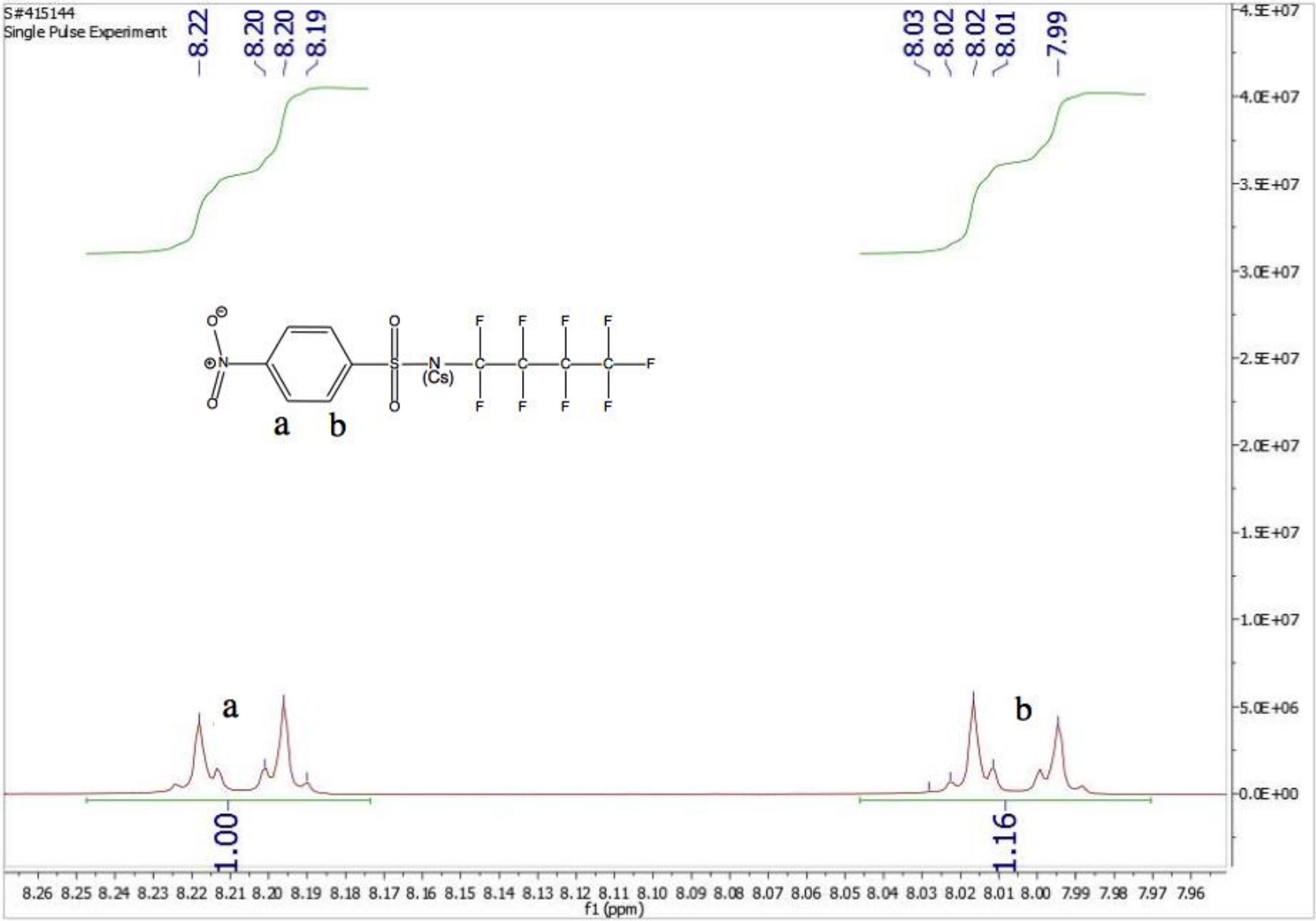
APPENDIX C: IR SPECTRUM OF COMPOUND I.



APPENDIX D: PROTON NMR SPECTRUM OF COMPOUND I.



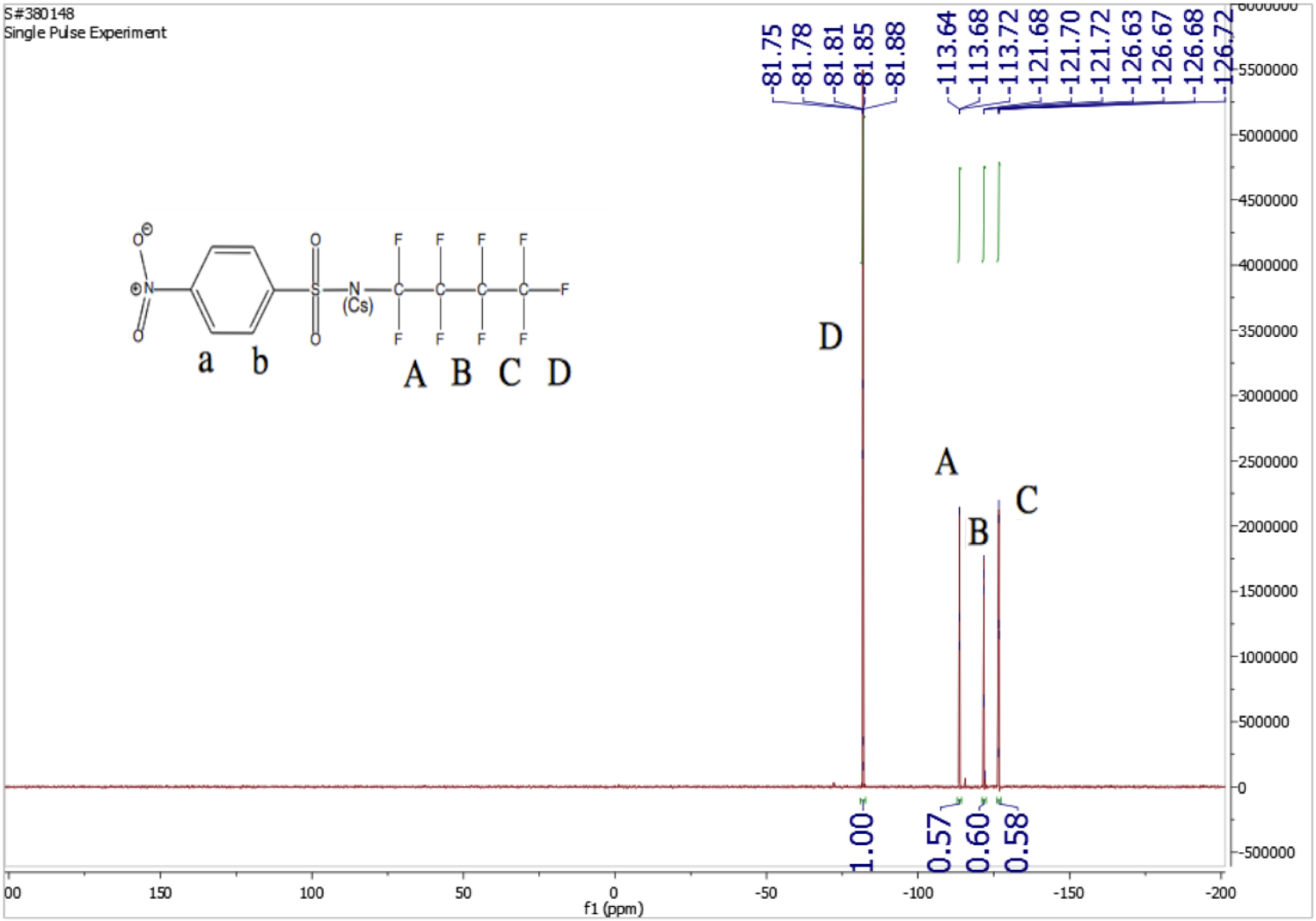
APPENDIX E: ENLARGED PROTON NMR SPECTRUM OF COMPOUND I (1).



APPENDIX E: ENLARGED PROTON NMR SPECTRUM OF COMPOUND I (2).

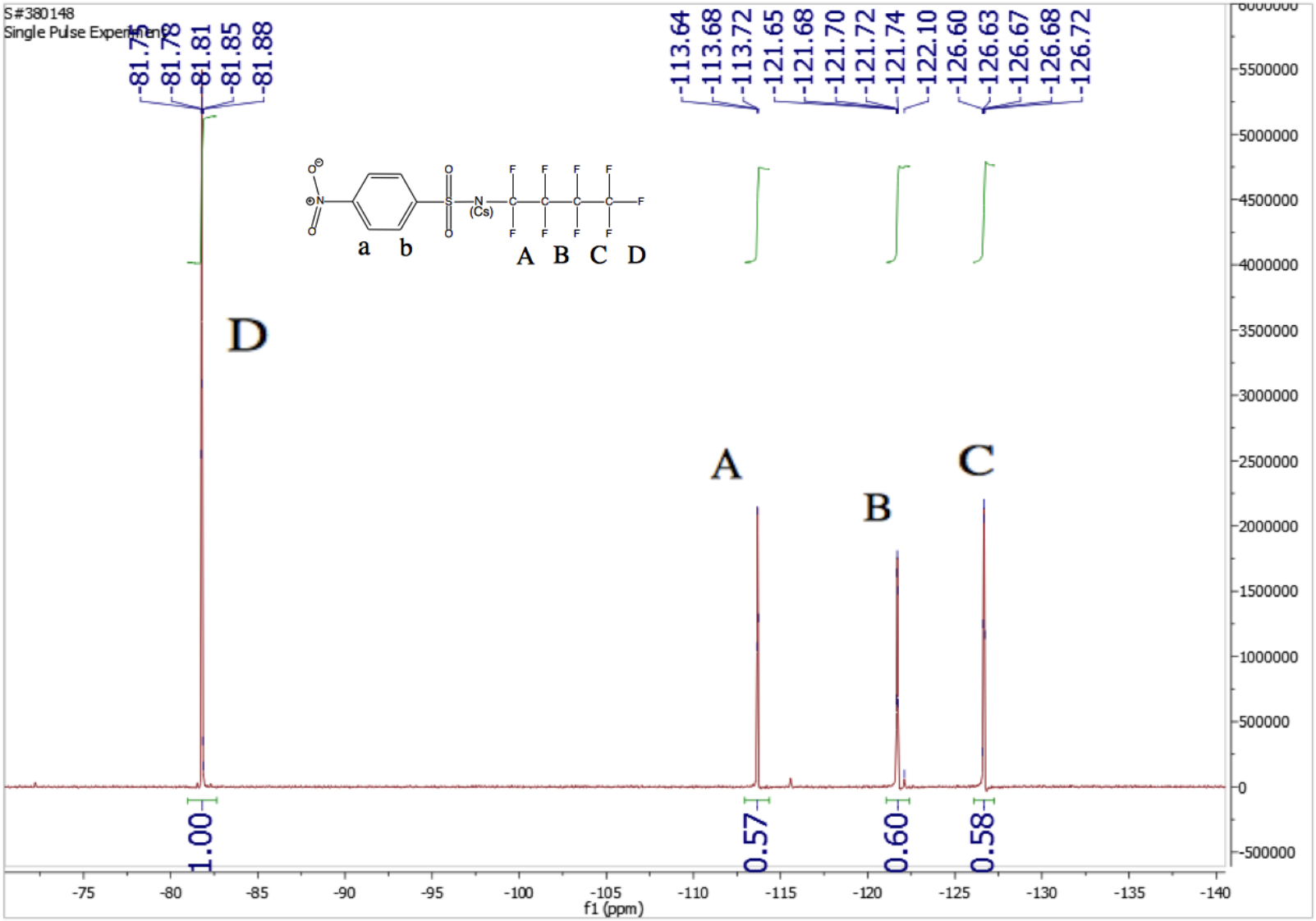
* These peaks are signals for the aromatic protons associated with the hydrolysis impurity

APPENDIX G: FLUORINE NMR SPECTRUM OF COMPOUND I.

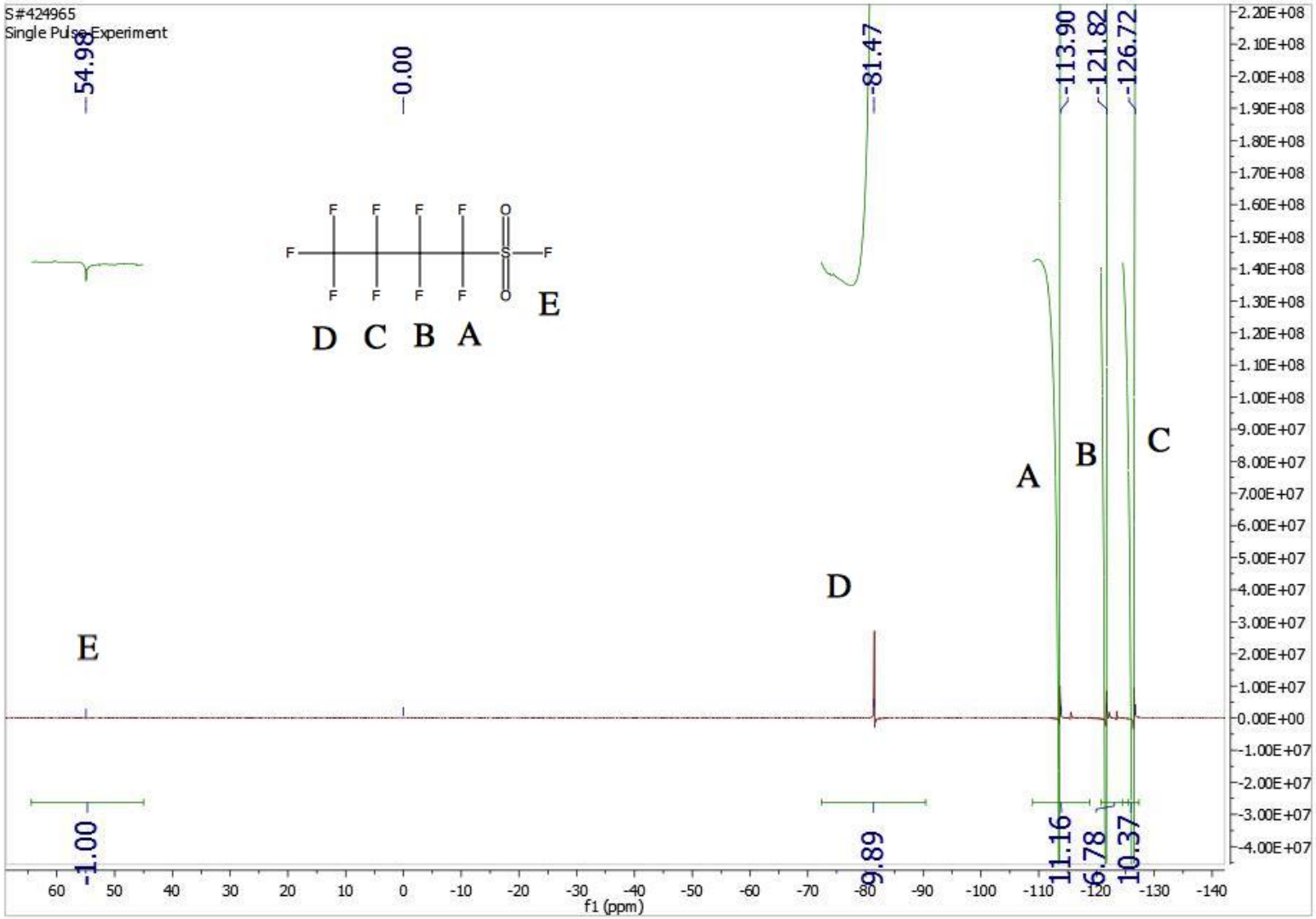


*No solvent peak is found on this spectrum.

APPENDIX H: ENLARGED FLUORINE NMR SPECTRUM OF COMPOUND I.



APPENDIX I: FLUORINE NMR SPECTRUM OF NONAFLUOROSULFONYL BUTANE.



* Spectrum of starting material shows 55.0 ppm peak of sulfonyl fluoride group. This sample is a liquid and required no solvent.

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